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# THE RAMAN AND INFRARED SPECTRA OF 2,4 AND 3,4-DICHLOROBENZYL CHLORIDE AND 1,2,4-TRIMETHYL BENZENE*

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Plate II

**ABSTRACT.** The Raman and infrared spectra of 2,4-dichloro-and 3,4-dichlorobenzyl chloride and 1,2,4-trimethyl benzene have been studied and assignments of the observed frequencies to different vibrational modes of the molecules have been proposed. The Raman spectra of the compounds in the solid state at $-180°C$ have also been investigated. In the case of the two isomeric dichlorobenzyl chlorides, some changes in some of the frequencies of the molecules are found to take place with solidification of the liquids. It has been concluded that the Cl atom of $CH_2Cl$ group in the 2,4-dichlorobenzyl chloride molecule forms weak bonds with H atoms of the neighbouring molecule, while such hydrogen bonding does not take place in the case of the 3,4-isomer. The reason has been discussed.

Small changes in the spectra are also observed in the case of 1,2,4-trimethyl benzene and it has been concluded that no new intermolecular bonding takes place in this case at the low temperature.

## INTRODUCTION

The Raman spectra of a large number of mono- and disubstituted benzenes in the solid state at low temperatures were studied by many previous workers (Biswas, 1954, 1955; Deb, 1960, 1961, 1962; Mukherjee, 1960) and those of some trisubstituted benzenes in the solid state at $-180°C$ have been studied by the present author (Deb, 1960). It has been observed that some of the intramolecular vibrational modes of the molecules are affected by change of state and a few low frequency Raman lines are exhibited by the compounds at low temperature, the number of such lines depending on the nature and relative positions of the substituents. In continuation of these investigations, the Raman and infrared spectra of 2,4-dichlorobenzyl chloride, 3,4-dichlorobenzyl chloride and 1,2,4-trimethyl benzene have been studied under different conditions. The states of polarization of the Raman lines have also been determined. The results have

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been discussed in the present paper and an attempt has been made to assign the observed frequencies to appropriate vibrational modes of the molecules.

## EXPERIMENTAL

The liquids 2,4-dichlorobenzyl chloride and 3, 4-dichlorobenzyl chloride supplied by Light and Co., England and 1, 2, 4-trimethyl benzene obtained from Eastman Kodak Co., U.S.A., were of chemically pure quality and they were further purified by distillation under reduced pressure. The arrangements for recording the Raman spectra in the liquid state and in the solid state at $-180°C$ and for studying the state of polarisation of the Raman lines in the liquid state were the same as those used earlier (Deb, 1960). The spectra were recorded on Ilford Zenith plates with the help of a Fuess glass spectrograph having a dispersion of about 11 Å/mm in the region 4047 Å.

The infrared spectra of the liquids were recorded in the region from 607 $cm^{-1}$ to 3600 $cm^{-1}$ with the help of a Perkin-Elmer Model 21 spectrophotometer with NaCl optics. Films of the liquids of thickness of a few microns enclosed between two NaCl discs were used in recording the spectra due to the liquids.

## RESULTS

The Raman spectra are shown in Figs. 1, 2 and 3, Plate II. The observed Raman shifts of the molecules in the liquid state and in the solid state at $-180°C$ are tabulated in Tables I, II and III. The Raman frequencies of 1, 2, 4-trimethyl benzene in the liquid state reported by previous workers are also included in Table III. The state of polarisation of the Raman lines of the liquids are indicated by the letters 'P' and 'D' which mean partially polarised and totally depolarised respectively.

The infrared absorption curves of the liquids are shown in Figs. 4, 5 and 6 and the frequencies of the observed bands are tabulated in Table IV.

## DISCUSSION OF RESULTS

### (a) *Assignments of the Raman lines*

The molecules of 2, 4-dichlorobenzyl chloride, 3, 4-dichlorobenzyl chloride and 1, 2, 4-trimethyl benzene belong to the point group $C_s$. In such molecules the polarised Raman frequencies would belong to the symmetry class $a'$ giving vibrations in the plane of the molecules while the depolarised Raman lines belong to the symmetry class $a''$ giving vibrations perpendicular to the plane of the molecule. Tentative assignments of the lines are given in the third column of Tables I and II and in the fourth column in Table III. The numbering of the modes of vibration has been made following that for the benzene ring made by Pitzer and Scott (1943).

It is seen from Table I, II and III that there are four totally depolarised Raman lines in the spectra due to 2, 4-dichlorobenzyl chloride and 3, 4-dichloro-

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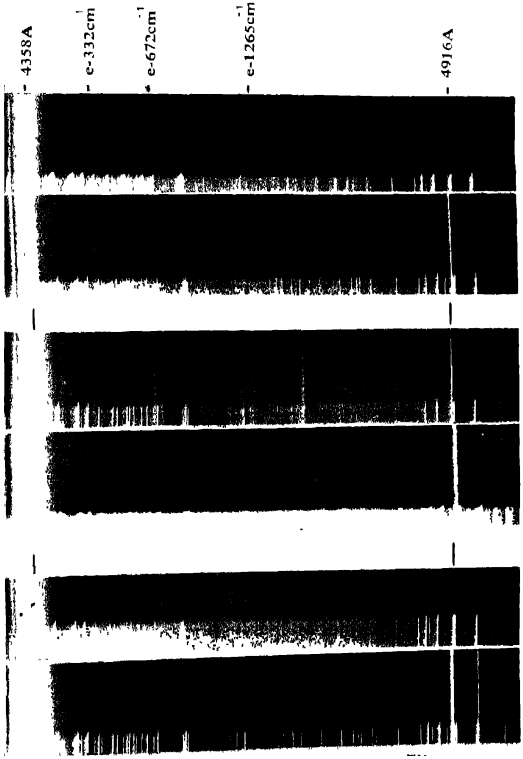


Fig 1.

Fig. 2

Fig. 3

Fig 1. (a) Raman spectrum of 2,4-dichlorobenzyl chloride, liquid at 32°C
(b) " " " Solid at – 180°C

Fig. 2. (a) Raman spectrum of 3,4-dichlorobenzyl chloride, liquid at 32°C.
(b) " " " " Solid at – 180°C

Fig. 3. (a) Raman spectrum of 1,2,4-trimethyl benzene, liquid at 32 C
(b) " " " " Solid at – 180°C.

benzyl chloride in the region below 400 $cm^{-1}$. As the molecules have no centre of symmetry, the out-of-plane degenerate mode No. 16 would be allowed and split up in these cases. The lines 171 and 98 $cm^{-1}$ of 2, 4-dichlorobenzyl chloride and the lines 155 and 95 $cm^{-1}$ of 3, 4-dichlorobenzyl chloride may correspond to the modes 16A and 16B of benzene. The Raman lines 210 and 182 $cm^{-1}$ of the first compound and 250 $cm^{-1}$ and 197 $cm^{-1}$ of the second compound probably represent the out-of-plane bending oscillations of both C-Cl and C-H bonds corresponding to the modes 10A and 10B respectively. The modes 16A and 16B in the case of 1, 2, 4-trimethyl benzene seem to give the lines 210 and 145 $cm^{-1}$ and the modes 10B and 10A probably give the lines 287 and 313 $cm^{-1}$ respectively.

TABLE I

Raman spectra of 2, 4-dichlorobenzyl chloride

| Raman shifts. in $cm^{-1}$ | | | | Symmetry class | Assignment Mode No (Pitzer and Scott, 1943) |
|---|---|---|---|---|---|
| Liquid at 30°C (Present author) | | Solid at − 180°C (Present author) | | | |
| 98 (2b) | D | 98 (2) | | a″ fundamental | 16 B |
| 171 (3) | D | 176 (1) | | a″ ,, | 16 A |
| 182 (3) | D | 183 (1) | | a″ ,, | 10 B |
| 210 (5) | D | 207 (1b) | | a″ ,, | 10 A |
| 259 (1b) | P | | | a′ ,, | 11 (C-Cl bending in $CH_2Cl$ gr.) |
| 332 (6) | P | 335 (0) | | a′ ,, | 6 A |
| 396 (4) | P | 396 (0) | | a′ ,, | 9 A |
| 461 (3) | P | 460 (0) | | a′ ,, | 6 B |
| 557 (3) | P | 557 (0) | | a′ ,, | 9 B |
| 650 (2) | D | 651 (0) | | a″ ,, | 17 B |
| 672 (12) | P | 664 (10) | | a′ ,, | 1 |
| 720 (6) | D | 718 (2) | | a″ ,, | 17 A |
| 737 (6) | P | 737 (2) | | a′ ,, | C-Cl stretching in $CH_2Cl$ group |
| 850 (3) | P | | | a′ ,, | 19 A |
| 1044 (2) | D | | | a′ ,, | 8 A |
| 1095 (4) | P | 1095 (0) | | a′ ,, | 19 B |
| 1145 (3) | P | 1149 (0) | | a′ ,, | 7A |
| 1214 (5) | P | 1218 (4) | | a′ ,, | 7 B |
| 1265 (8) | P | 1265 (2) | | a′ ,, | 2 |
| 1296 (0) | | 1296 (0) | | | |
| 1386 (0) | | | | | |
| 1444 (1) | | | | | $CH_2$ bending oscillation in $CH_2Cl$ group |
| 1584 (12) | D | 1584 (6) | | a′ ,, | 8 B |
| 2968 (2b) | P | 2968 (1b) | | | $CH_2$ stretching oscillation in $CH_2Cl$ gr. |
| 3065 (4b) | P | 3064 (0) | | a′ ,, | CH valence oscillation, 7 B and 2 superposed |

TABLE II

Raman spectra of 3, 4-dichlorobenzyl chloride

| Raman shifts in $cm^{-1}$ | | Symmetry class | | Assignment Mode No. (Pitzer and Scott, 1943) |
|---|---|---|---|---|
| Liquid at 30°C (Present author) | Solid at −180°C (Present author) | | | |
| 95 (2b) D | 95 (2) | a″ | fundamental | 16 B |
| 155 (6b) D | 155 (2b) | a″ | ,, | 16 A |
| 197 (5) D | 197 (0b) | a″ | ,, | 10 B |
| 250 (1b) D | 245 (0) | a″ | ,, | 10 A, C-Cl bending in $CH_2$ Cl group |
| 333 (6) P | 336 (1) | a′ | ,, | 6 A |
| 425 (3) P | 425 (0) | a′ | ,, | 9 A |
| 465 (8) P | 465 (1) | a′ | ,, | 6 B |
| 556 (4) P | 556 (1) | a′ | ,, | 9 B |
| 661 (1) D | 666 (0) | a″ | ,, | 17 B |
| 680 (10) P | 683 (8) | a′ | ,, | 1 |
| 695 (1) D | 695 (0) | a″ | ,, | 17 A |
| 722 (8b) P | 722 (3) | a′ | ,, | C-Cl stretching in $CH_2Cl$ group |
| 831 (0b) P | | | | |
| 879 (3b) P | 879 (0b) | a′ | ,, | 19 A |
| 1034 (8) P | 1034 (2) | a′ | ,, | 19 B |
| 1140 (8) P | 1140 (1) | a′ | ,, | 7 A |
| 1215 (10) P | 1217 (6) | a′ | ,, | 7 B |
| 1276 (8b) P | 1276 (3b) | a′ | ,, | 2 and 8A superposed |
| 1446 (1) | | | | $CH_2$ bending oscillation in $CH_2Cl$ group |
| 1593 (15) D | 1595 (6) | a′ | ,, | 8 B |
| 2964 (4b) P | 2964 (0b) | | | $CH_2$ stretching oscillation in $CH_2Cl$ group |
| 3060 (6b) P | 3064 (0b) | a′ | ,, | CH valence oscillation, 7 B and 2 superposed |

TABLE III

Raman spectra of 1, 2, 4-trimethyl benzene

| Raman shifts in $cm^{-1}$ | | | | Assignment |
|---|---|---|---|---|
| Pure liquid | | Solid at −180°C Present author | Symmetry class | Assignment Mode No. (Pitzer and Scott, 1943) |
| Landolt-Börnstein Tables (1951) | Present author | | | |
| 148 (2) | 145 (0b)D | 150 (1) | a″ fundamental | 16 B |
| 207 (4,7) D | 210 (4b)D | 212 (1) | a″ ,, | 16 A |
| 232 (1) | 237 (1) D | 238 (1) | a″ ,, | 11 |
| 281 (2,0)P | 287 (1) D | | a″ ,, | 10 B |
| 318 (23,6)D | 313 (6)D | 313 (2) | a″ ,, | 10 A |
| 434 (6,4)P | 437 (1)P | | a′ ,, | 9 A |
| 470 (19,8)P | 475 (5)P | 475 (2) | a′ ,, | 6 A |
| 515 (1) | | | | |
| 537 (1) | 538 (0) | | | |
| 554 (29,6)P | 558 (6) P | 558 (3) | a′ ,, | 6 B |
| 576 (2) | | | | |
| 603 (1,3) P | | | | |
| 686 (6,0)P | | | | |
| 716 (20,8) P | 719 (3) P | 718 (0) | a′ ,, | 9 B |
| 743 (47,7) P | 747 (10) P | 747 (4) | a′ ,, | 1 |
| 806 (1,7) P | 806 (0b) P | | | |
| 871 (1,6) P | 874 (0) P | | | |
| 924 (14,6) P | 928 (4) P | 926 (0) | a′ ,, | 19 A |
| 1023 (3,1) P | 1020 (0vb) | | | |
| 1095 (2) | | | | |
| 1124 (4,3) | 1123 (2) P | 1125 (2) | a′ ,, | 19 B |
| 1148 (3,5) | | | | |
| 1157 (2) | 1160 (1) P | 1167 (2) | a′ ,, | 7 A |
| 1188 (2,3) | | | | |
| 1209 (4,0) | 1213 (1) P | | | |
| 1243 (33,6) P | 1246 (12) P | 1243 (8) | a′ ,, | 2 |
| 1379 (25,4) P | 1383 (8) P | 1383 (2) | a′ ,, | 7 B |
| 1444 (12,0) | 1448 (4b) P<br>1545 (0) | 1448 (2) | | CH bending in $CH_3$ group |
| 1576 (6,5) P | 1582 (1) D | | a′ ,, | 8 A |
| 1618 (20,0) P | 1620 (8) D | 1616 (6) | a′ ,, | 8 B |
| 2731 (1) | 2736 (1) P | | | |
| 2857 (3) | 2859 (4) P | 2860 (1) | | CH oscillation in $CH_3$ group |
| 2912 (6b) | 2918 (8b) P | 2911 (4b) | | CH oscillation in $CH_3$ group |
| 3038 (3) | 3040 (6) P | 3035 (2) | a′ ,, | CH valence oscillation, 7 B and 2 superposed |

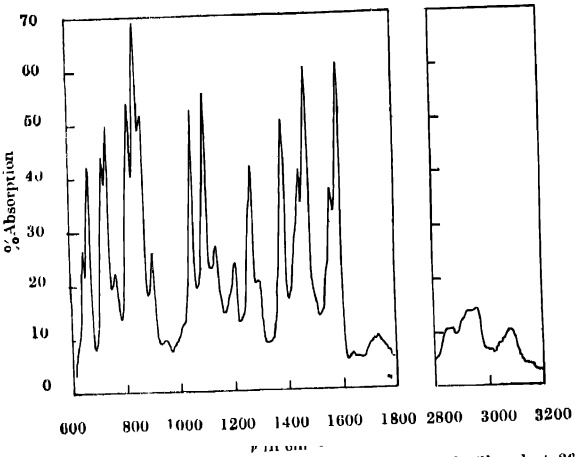


Fig. 1. Infra-red spectrum of 2 4 dichloro benzyl chloride (liquid at 26°C)

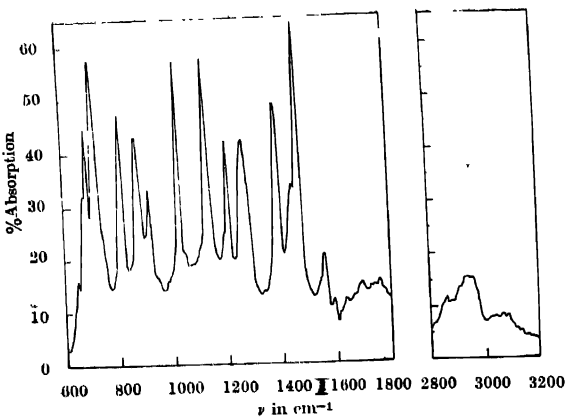


Fig. 5. Infra-red spectrum of 3, 4 dichloro benzyl chloride (liquid at 26°C).

TABLE IV

Infrared spectra of 2, 4-dichloro- and 3, 4-dichlorobenzyl chloride and 1, 2, 4-trimethyl benzene. Infra-red bands Wave number in $cm^{-1}$ and Intensity

| 2,4-dichlorobenzyl chloride | 3,4-dichlorobenzyl chloride | 1,2,4-trimethyl benzene |
|---|---|---|
| 650 (w) | 650 (vw) | |
| 672 (ms) | 670 (w) | |
| | 688 (ms) | 700 (w) |
| 725 (ms) | 718 (s) | |
| 742 (s) | | 742 (ms) |
| 770 (vw) | | 760 (vw) |
| 822 (s) | 815 (ms) | 800 (vs) |
| 848 (vs) | | |
| 870 (s) | 875 (ms) | 870 (ms) |
| 906 (w) | 920 (w) | 998 (ms) |
| 1012 (vw) | 1028 (s) | 1020 (ms) |
| 1055 (s) | | 1030 (ms) |
| 1101 (s) | 1130 (s) | 1120 (w) |
| 1140 (w) | 1190 (vw) | 1170 (vw) |
| 1210 (w) | 1206 (ms) | 1210 (w) |
| 1260 (ms) | 1255 (ms) | 1210 (w) |
| 1272 (ms) | 1265 (ms) | 1250 (w) |
| 1300 (w) | 1285 (w) | 1330 (w) |
| 1365 (w) | | |
| 1390 (s) | 1390 (ms) | 1380 (ms) |
| 1435 (ms) | | 1420 (ms) |
| 1450 (ms) | 1442 (w) | 1450 (vs) |
| 1465 (ms) | | 1465 (s) |
| | 1470 (vs) | |
| 1480 (s) | | 1500 (s) |
| 1545 (w) | 1540 (vw) | 1530 (w) |
| 1565 (ms) | 1560 (vw) | 1550 (w) |
| 1593 (s) | 1590 (vw) | 1570 (w) |
| | | 1610 (ms) |
| | | 2730 (vw) |
| 2862 (w) | 2855 (w) | 2865 (vs) |
| | 2900 (w) | |
| 2930 (w) | 2940 (w) | 2930 (vs) |
| 2960 (w) | | 3010 (vs) |
| 3060 (w) | 3058 (vw) | |

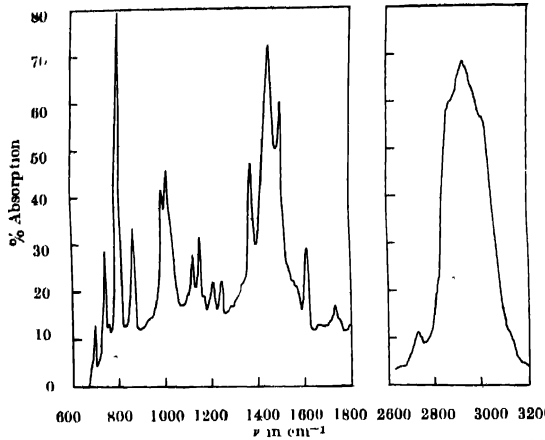


Fig. 6. Infra-red spectrum of 1, 2, 4 trimethyl benzene (liquid at 26°C.)

The degenerate mode No. 6 of benzene representing the in-plane bending oscillation of the carbon ring may correspond to the frequencies 332 and 461 $cm^{-1}$ in the case of 2, 4-dichlorobenzyl chloride and to 333 and 465 $cm^{-1}$ of 3, 4-dichlorobenzyl chloride. In the case of 1, 2, 4-trimethyl benzene the modes 6A and 6B probably give the lines 475 and 558 $cm^{-1}$ respectively. The frequencies corresponding to the modes 8A and 8B may account for the lines 1044 and 1584 $cm^{-1}$ respectively in the case of 2, 4-dichlorobenzyl chloride. The lines 1593 $cm^{-1}$ in the case of 3, 4-dichlorobenzyl chloride corresponds to the mode 8B and the frequency corresponding to the mode 8A is probably superposed on the mode No. 2 of benzene giving a strong and broad line at 1276 $cm^{-1}$. The lines 1582 and 1620 $cm^{-1}$ in the case of 1,2,4 trimethyl Benzene probably account for the modes 8A and 8B respectively. In the last case, in the mode 8A, the two diametrically opposite CH groups may be displaced simultaneously towards the centre of the molecule and in that case the freuency will not be much different from that of the corresponding mode 18B of the benzene molecule.

The superposition of the modes 7A and 2 give rise to a pure CH valence oscillation in two diametrically opposite C-H groups in the three molecules and gives the lines 3065, 3060 and 3040 $cm^{-1}$ respectively in the three cases. The $CH_2$ valence oscillation in the $CH_2Cl$ and $CH_3$ groups give the lines 2960, 2964 and 2918 $cm^{-1}$ respectively. The other lines are assigned to different modes as shown in the Tables.

(b) *Changes in the Raman spectra with the solidification of the liquids*

It can be seen from Tables I and II that when 2, 4-dichloro and 3, 4-dichlorobenzyl chloride are solidified and cooled to −180°C, the Raman lines 332, 1265

and 3065 $cm^{-1}$ due to the former liquid and the lines 197, 333 and 1034 $cm^{-1}$ due to the latter liquid become much weaker. Probably, these lines being highly polarised, they are partly absorbed while traversing the polycrystalline mass. Further, in the case of 2, 4 dichlorobenzyl chloride the line 672 $cm^{-1}$ shifts to 664 $cm^{-1}$ with solidification of the substance. This may be due to the formation of a weak bond between Cl atom of the $CH_2Cl$ group and hydrogen atom of the neighbouring molecule. In the case of 3, 4-dichlorobenzyl chloride, however, no such shift of the line 680 $cm^{-1}$ takes place. This may be explained on the assumption that the Cl atom in the $CH_2Cl$ group is attached to the adjacent H atom in the same molecule so that it is no longer able to form intermolecular bond.

Small changes also occur in the case of 1, 2, 4-trimethyl benzene as can be seen from Table III. The line 1160 $cm^{-1}$ corresponding to the mode 7A shifts to 1167 $cm^{-1}$ and increases in intensity when the compound is solidified and cooled to $-180°C$. Also, the line 210 $cm^{-1}$ due to a C—H out-of-plane bending oscillation becomes weaker under similar condition. These changes are obviously due to influence of crystal field on the molecule. The electronic spectra do not undergo any drastic change with the solidification of the liquid (Misra, 1962) and therefore, no new intermolecular bond-formation takes place in this case.

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